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12,13-*iso*-Baccatin III. Taxane Enol Esters (12,13-*iso*-Taxanes)

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Supporting Information

7-O-Triethylsilyl-12,13-*iso*-baccatin III (5). Zinc dust[†] (56 g) was activated by sequential washing with 1 N HCl, deionized water (5x), methanol (4x) and ethyl ether (3x). The zinc was vacuum dried and maintained under nitrogen. A small flask was charged with 13-keto-7-O-TES-baccatin III (5 g), glacial acetic acid (40 mL) and activated zinc (36 g). The reaction was stirred, excluding air, for 3.5 h. The reaction was diluted with nitrogen-purged ethyl acetate and filtered through diatomaceous earth. Nitrogen-purged toluene was added and the mixture was evaporated under reduced pressure to give a white solid. The solid was stored at room temperature under an inert atmosphere. The solid has the following analytical properties: IR (Nujol) 3508, 3402, 1741, 1725, 1716, 1687, 1439, 1315, 1303, 1281, 1241, 1112, 1102, 982, 821, 815, 744 cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 8.08 (d, 2H, J = 7.1 Hz); 7.61 (m, 1H); 7.48 (m, 2H); 5.91 (s, 1H); 5.48 (dd, 1H); 4.93 (dd, 1H); 4.39 (d, 1H, J = 8.4 Hz); 4.37 (s+m, 2H); 4.25 (d, 1H, J = 8.4 Hz); 4.14 (d, 1H, J = 5.3 Hz); 2.74 (d, 1H, J = 18 Hz); 2.50 (m, 2H); 2.33 (s, 3H); 2.18 (s, 3H); 2.09 (d, 1H, J = 18 Hz); 1.87 (m, 1H); 1.82 (s, 3H); 1.61 (s, 3H); 1.14 (s, 3H); 1.11 (s, 3H); 0.89 (m, 9H); 0.53 (m, 6H); ^{13}C NMR

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($CDCl_3$, TMS) δ 205.5, 170.8, 168.8, 166.6, 146.0, 133.6, 129.9, 129.0, 128.5, 102.4, 84.5, 80.9, 76.8, 75.6, 73.4, 73.1, 59.1, 56.5, 39.7, 38.6, 37.2, 32.4, 29.9, 23.1, 21.2, 18.8, 12.8, 9.1, 6.7, 5.4.

Anal: Calc for $C_{37}H_{52}O_{11}Si_1$: C, 63.41; H, 7.48; Found: C, 63.31; H, 7.45.

[†]Zinc dust lots having particle sizes of less than 10 microns were activated by grinding under 1 N HCl in a mortar, followed by the washings described above.

(12*R*)-7-O-Triethylsilyl-11,12-dihydro-13-keto-baccatin III (4). Enol **5** (0.10 g) was chromatographed on silica gel 60 (230-400 mesh, 10 g) in (20-80) to (40-60) EtOAc-hexane. Fractions were of 5 mL. The desired product was found in fractions 20-42. A 77% yield (77 mg) of product plus starting material was obtained. Retreatment of the mixture with silica gel in a scintered glass funnel produced nearly pure **4**. The conversion may also be accomplished on a preparative thin layer silica gel plate. ^1H NMR ($CDCl_3$, TMS) δ 8.12 (d, 2H, J = 8.5 Hz); 7.62 (m, 1H); 7.50 (m, 2H); 5.69 (d, 1H, J = 7.4 Hz); 5.42 (d, 1H, J = 4.9 Hz); 5.00 (dd, 1H); 4.65 (m, 1H); 4.39 (d, 1H, J = 9.0 Hz); 4.29 (d, 1H, J = 9.3 Hz); 3.19 (m, 1H); 3.08 (d, 1H, J = 16 Hz); 2.83 (d, 1H, J = 7.5 Hz); 2.48 (s+m, 5H); 2.39 (d, 1H, J = 17 Hz); 2.06 (s, 3H); 1.96 (s, 1H); 1.82 (m, 2H); 1.60 (s, 3H); 1.46 (s, 3H); 1.19 (s, 3H), 1.02 (d, 3H, J = 7 Hz); 0.90 (m, 9H); 0.52 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS) δ 207.8, 206.3, 170.2, 167.8, 167.2, 133.8, 130.0, 128.7, 128.6, 83.8, 81.8, 79.5, 76.9, 73.3, 70.5, 69.9, 57.3, 56.1, 45.5, 44.6, 41.5, 40.9, 36.2, 33.2, 23.3, 22.1, 21.0, 10.9, 9.6, 6.9, 5.9; mass spectrum (FAB) 701.3369, $C_{37}H_{52}O_{11}Si+H_1$ requires 701.3357 m/z.

7-O-Triethylsilyl-11,12-dihydro-12β-hydroperoxy-13-ketobaccatin III (6). Enol **5** (0.1 g) was dissolved in CH_2Cl_2 and shaken well in a separatory funnel with 1 N hydrochloric acid.[‡] The CH_2Cl_2 solution was dried over anhydrous Na_2SO_4, filtered,

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and evaporated. The product was crystallized from CH_2Cl_2-hexane to give 7-TES-11,12-dihydro-12-hydroperoxy-13-keto-baccatin III. ^1H NMR ($CDCl_3$, TMS) δ 8.79 (bs, 1H); 8.11 (d, 2H, J = 7 Hz); 7.61 (m, 1H); 7.48 (m, 2H); 5.68 (d, 1H, J = 7.4 Hz); 5.55 (d, 1H, J = 3.7 Hz); 4.93 (dd, 1H); 4.50 (m, 1H); 4.35 (d, 1H, J = 8.5 Hz); 4.28 (d, 1H, J = 8.4 Hz); 3.05 (d, 1H, J = 16 Hz); 2.87 (d, 1H, J = 16 Hz); 2.69 (d, 1H, J = 7.5 Hz); 2.64 (d, 1H, J = 3.8 Hz); 2.51 (m, 1H); 2.44 (s, 3H); 2.10 (s, 3H); 2.01 (s, 1H); 1.85 (m, 1H); 1.49 (s, 3H); 1.46 (s, 3H); 1.14 (s, 3H); 0.92 (s, 3H); 0.89 (m, 9H); 0.51 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS) δ 204.6, 204.4, 170.6, 168.0, 166.9, 133.8, 130.0, 128.9, 128.6, 89.1, 83.8, 81.7, 79.7, 77.0, 73.2, 72.5, 70.6, 57.8, 57.4, 42.4, 41.6, 40.3, 36.4, 33.4, 24.8, 22.3, 20.9, 16.9, 9.9, 6.8, 5.7; mass spectrum (FAB) 733.3230, $C_{37}H_{52}O_{13}Si+H_1$ requires 733.3255 m/z.

‡The rate at which **5** is converted to **6** varies considerably from experiment to experiment (from about 0.5 hr to 12-24 hr). As yet, we do not completely understand the reason(s) for this variability.

7-O-Triethylsilyl-11,12-dihydro-12β-hydroxy-13-ketobaccatin III (7). Enol **5** (150 mg, 0.21 mM) was dissolved in CH_2Cl_2 (2 mL) and treated with 85% *m*-chloroperoxybenzoic acid (188 mg, 0.90 mM). The solution was purged with N_2, then stirred at room temperature overnight. The reaction was diluted with CH_2Cl_2 and washed with 5% $Na_2S_2O_3$ and 5% $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel 60 (230-400 mesh, 15 g) in (20-80) ethyl acetate-toluene. Fractions of 5 mL were collected. The desired product (21 mg, 14%) was found in fractions 17-22; ^1H NMR ($CDCl_3$, TMS) δ 8.08 (d, 2H, J = 6 Hz), 7.63 (m, 1H), 7.50 (m, 2H), 5.92 (d, 1H, J = 3Hz), 5.72 (d, 1H, J = 5.3 Hz), 4.95 (dd, 1H), 4.63 (dd, 1H), 4.37 (AB, 2H), 2.99 (d, 1H, J = 13.3 Hz), 2.93

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(d, 1H, J = 5.3 Hz), 2.70 (d, 1H, J = 13.2 Hz), 2.71 (s, 1H), 2.64 (d, 1H, J = 3 Hz); 2.55 (m, 1H), 2.34 (s, 3H), 2.15 (s, 3H), 1.94 (m, 1H), 1.86 (s, 1H), 1.68 (s, 3H), 1.53 (s, 3H), 1.29 (s, 3H), 1.17 (s, 3H), 0.92 (t, 9H), 0.55 (q, 6H); ^{13}C NMR ($CDCl_3$, TMS) δ 211.3, 204.9, 170.7, 168.4, 166.8, 133.9, 130.0, 129.0, 128.8, 83.9, 81.3, 80.8, 77.4, 73.8, 73.5, 70.6, 60.6, 57.5, 42.4, 41.9, 40.9, 36.7, 31.9, 25.7, 23.8, 22.1, 21.1, 10.2, 6.9, 5.8; mass spectrum (FAB) 717.3295, $C_{37}H_{52}O_{12}Si+H_1$ requires 717.3306 m/z.

7-O-Triethylsilyl-11,12-dihydro-12β-hydroxy-baccatin III (8). A. From Reduction of 6. A solution of the ketone **6** (0.091 mM) in CH_2Cl_2 (1 mL) was treated with tetrabutylammonium borohydride (50.8 mg, 0.197 mM). The reaction was stirred at room temperature 40 minutes. The reaction was quenched with acetic acid (0.1 mL) and stirred 15 minutes. The mixture was then partitioned between 5% aqueous $NaHCO_3$ and CH_2Cl_2. The organic layer was dried and evaporated. The crude product was purified by column chromatography on silica gel 60 (6 g, 230-400 mesh) in (20-80), (40-60), and (50-50) EtOAc-toluene. Fractions of 3 mL were collected. The desired product (32.5 mg, 50%) was found in fractions 28-30. Crystallization from CH_2Cl_2-hexane gave colorless crystals, mp 208-209°C; ^{1}H NMR ($CDCl_3$, TMS) δ 8.17 (d, 2H, J = 8.6 Hz); 7.60 (m, 1H); 7.48 (m, 2H); 5.97 (d, 1H, J = 5.8 Hz); 5.66 (d, 1H, J = 8.6 Hz); 5.06 (dd, 1H); 4.59 (m, 2H); 4.36 (d, 1H, J = 8.3 Hz); 4.30 (d, 1H, J = 8.2 Hz); 3.72 (m, 1H); 2.89 (bs, 1H); 2.56 (m, 1H); 2.38 (d, 1H, J= 16.0 Hz); 2.24 (s+m, 5H); 2.08 (s+m, 4H); 1.85 (m, 1H); 1.77 (s, 1H); 1.68 (s, 3H); 1.62 (s, 1H); 1.37 (s, 3H); 1.33 (s, 3H); 1.10 (s, 3H), 0.93 (t, 9H); 0.53 (q, 6H); ^{13}C NMR ($CDCl_3$, TMS) δ 206.5, 170.0, 168.6, 167.3, 133.2, 129.9, 129.6, 128.3, 83.6, 80.4, 79.7, 77.0, 76.3, 75.3, 74.3, 73.5, 72.7, 70.3, 58.4, 56.9, 39.8, 39.7, 36.1, 34.5, 32.3, 27.6, 26.4, 22.1, 21.2, 9.8, 6.8, 5.9.

Single-crystal structure determination: $C_{37}H_{54}O_{12}Si_1$; Space group: $P2_12_12_1$; cell

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parameters: *a=8.559(5)*Å, *b=16.494(4)*Å, *c=31.453(9)*Å; molecular weight = 718.914; Z=4; calculated density = 1.0777g/cm^3. A clear chunky crystal was selected and mounted on a glass fiber. The data were collected on a Siemens $P2_1$ X-ray diffractometer controlled by a Harris computer, at low temperature (-130°C), with graphite-monochromatized CuKα radiation [λ(CuKα)=1.5405Å]. All 4120 unique reflections were measured to a $2\theta_{max}$ of 136° for Laue group mmm; 2481 intensities were > 3σ. The structure was solved by direct methods, using SHELX-86.[25] The trial solution obtained 49 nonhydrogen atoms. Least squares refinements included all nonhydrogen atomic coordinates and isotropic thermal parameters. Some disorder solvent molecules (12 nonhydrogen atoms), found on the Fourier map, were included in the refinements. These atoms refined to stabilized temperature factors also. In the final refinement cycle, all shifts were <0.38σ for nonhydrogen atoms. With all 4120 reflections: R=0.148, S=2.69, Rw=0.267; with 2481 reflections have intensities > 3σ: R=0.112. The CRYM system of computer programs was used.[26]

B. From Reduction of 7. Dry $CeCl_3$ (29 mg, 0.12 mM) was dissolved in CH_3OH (0.3 mL). This solution was added to 7-triethylsilyl-11,12-dihydro-12β-hydroxy-13-ketobaccatin III (**7**) (0.01 mg, 0.014 mM) along with CH_2Cl_2 (0.2 mL). Solid $NaBH_4$ (32 mg, 0.85 mM) was added to the reaction, causing vigorous bubbling. When the bubbling stopped, the reaction was partitioned between EtOAc and 1N HCl. The organic layer was dried and evaporated to give 7-triethylsilyl-11,12-dihydro-12β-hydroxybaccatin III (**8**) having nmr data identical to that of the product of tetrabutylammonium borohydride reduction of hydroperoxide **6**.

7-O-Triethylsilyl-12,13-*iso*-baccatin III-13-(4S,5R)-N-(*t*-butyloxycarbonyl)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidinecarboxylic Acid Ester (10). A

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suspension of (4S,5R)-N-(BOC)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidinecarboxylic acid potassium salt (946 mg of 74% pure potassium salt, 1.5 mM) in EtOAc was washed with 5% aqueous $NaHSO_4$. The aqueous layer was extracted twice with EtOAc and the combined EtOAc solutions were dried over anhydrous Na_2SO_4 and evaporated to give the free acid as a thick oil. It was used immediately in the coupling reaction. A solution of (4S,5R)-N-(BOC)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidinecarboxylic acid (1.5 mM) in CH_2Cl_2 (2 mL) was treated with 4-dimethylaminopyridine (48 mg) and a solution of the enol (**5**) (0.492 g, 0.702 mM) in toluene (5 mL) plus CH_2Cl_2 (8 mL). Solid 1,3-dicyclohexylcarbodiimide (0.3316 g, 1.53 mM) was added and the reaction was stirred under an inert atmosphere for 2.5 h. The reaction was diluted with EtOAc and washed with aqueous $NaHSO_4$ followed by aqueous $NaHCO_3$ plus brine. The layers were filtered and separated and the organic layer was dried over anhydrous Na_2SO_4. The EtOAc solution was concentrated and chromatographed on silica gel 60 (230-400 mesh, 100 g) in (20-80) and (30-70) acetone-hexane. Fractions of 15 mL were collected. The desired product as a mixture of diastereomers (0.694 g, 89%) was found in fractions 34-44; ^1H NMR ($CDCl_3$, TMS) δ 8.02 (m, 2H); 7.3-7.7 (m, 8H); 6.71 (s, <1H); 6.45 (m, 2H); 5.99 (s, <1H); 5.88 (s, <1H); 5.52 (m, 1H); 5.30 (m, 1H); 4.88 (m, 1H); 4.30 (m, 2H); 3.89, 3.86, 3.83 (s's, 7H); 2.50 (m, 2H); 2.19, 2.16, 2.15 (s's, 5H); 1.85 (s+m, 4H); 1.61, 1.59, 1.53 (s's, 3H); 1.29, 1.25, 1.16, 1.11, 1.05 (s's, 15H); 0.91 (m, 9H); 0.53 (m, 6H).

N-Debenzoyl-N-(*t*-butyl)oxycarbonyl-12,13-*iso*-taxol (12). The 7-O-TES-2'-aminal (**10**) (0.69 g, 0.62 mM) was stirred in a mixture of HOAc (16 mL) and H_2O (4 mL) at room temperature under an inert atmosphere for 4 days. The reaction was diluted with EtOAc and washed multiple times with water and aqueous Na_2CO_3. The organic

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layer was dried over anhydrous Na_2SO_4 and evaporated. The product was chromatographed on silica gel 60 (230-400 mesh, 100 g) in (40-60) acetone-hexane. Fractions of 20 mL were collected. The desired product, not completely pure, was found in fractions 7-17. It was rechromatographed as above in (20-80) to (40-60) acetone-hexane. The desired product (0.24 g, 40%) was found in fractions 117-128; ^{1}H NMR($CDCl_3$, TMS) δ 8.13 (d, 2H, J = 7 Hz); 7.30-7.67 (m, 8H); 5.58 (d, 1H, J = 6 Hz); 5.48 (s, 1H); 5.40 (m, 1H); 4.94 (dd, 1H); 4.70 (d, 1H); 4.42 (d, 1H, J = 8 Hz); 4.36 (m, 1H); 4.33 (d, 1H, J = 8 Hz); 3.71 (d, 1H, J = 6 Hz); 3.52 (d, 1H, J = 4 Hz); 3.21 (bs, 1H); 2.92 (d, 1H, J =19 Hz); 2.76 (s, 1H); 2.57 (s, 3H); 2.51 (m, 1H); 2.23 (s, 3H); 2.08 (d, 1H, J =19 Hz); 1.92 (m, 1H); 1.30 (s, 3H); 1.22 (s, 9H); 1.06 (s, 3H); ^{13}C NMR ($CDCl_3$, TMS) δ 206.6, 172.0, 170.9, 170.7, 166.8, 155.2, 143.3, 138.5, 133.7, 130.3, 129.0, 128.9, 128.7, 128.0, 126.6, 121.9, 84.6, 81.0, 80.2, 77.8, 77.7, 73.7, 73.6, 71.5, 57.9, 55.7, 39.5, 38.8, 35.3, 32.7, 31.6, 29.8, 28.1, 22.6, 21.1, 20.0, 14.4, 9.1; mass spectrum (FAB) 850.3655, $C_{45}H_{55}NO_{15}+H_1$ requires 850.3650.

(12*R*)-7-O-Triethylsilyl-11,12-dihydrobaccatin III (13). The ketone **4** (0.123 g, 0.175 mM) was treated with CH_2Cl_2 (2 mL), a solution of cerium(III) chloride (220 mg, 0.89 mM) in MeOH, and sodium borohydride (211 mg, 5.6 mM). Vigorous bubbling ensued. When the bubbling slowed, the reaction was diluted with EtOAc and washed with dilute HCl. The aqueous was re-extracted twice and the combined organic layers were dried and evaporated. The product was adsorbed from MeOH-CH_2Cl_2 onto silica gel (2 g). This was placed on a column of 230-400 mesh silica gel (10 g) made up in (20-80) EtOAc-toluene. The column was eluted with (20-80) and (40-60) EtOAc-toluene. The desired product (**13**, 0.070 g, 58%) was found in fractions 40-59 and had mp 185-188°C; ^{1}H NMR ($CDCl_3$, TMS) δ 8.17 (d, 2H, J = 8 Hz); 7.60 (m, 1H); 7.48

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(m, 2H); 6.36 (d, 1H, J = 8.4 Hz); 5.63 (d, 1H, J = 8.5 Hz); 5.13 (dd, 1H); 4.66 (m, 1H); 4.53 (d, 1H, J = 8.5 Hz); 4.31 (AB, 2H); 3.99 (m, 1H); 2.58 (m, 1H); 2.50 (d, 1H, J = 16 Hz); 2.38 (m, 2H); 2.25 (s, 3H); 2.07 (s+m, 4H); 1.81 (s+m, 6H); 1.16 (s, 3H); 1.10 (s, 3H), 0.96 (d, 3H, J = 7.2 Hz); 0.93 (t, 9H); 0.52 (q, 6H); ^{13}C NMR ($CDCl_3$, TMS) δ 208.0, 169.8, 168.7, 167.6, 133.4, 130.1, 129.7, 128.5, 83.7, 80.2, 79.7, 76.8, 73.6, 71.4, 70.6, 70.3, 56.8, 53.6, 40.43, 40.38, 36.1, 35.3, 32.8, 32.6, 25.2, 22.2, 21.4, 14.4, 9.6, 7.0, 6.1; mass spectrum (FAB) 703.3506, $C_{37}H_{54}O_{11}Si$ requires 703.3513, other ions at 503, 115, 105 m/z.

(12*R*)-11,12-Dihydrobaccatin III (14). A solution of (12*R*)-7-triethylsilyl-11,12-dihydrobaccatin III (**13**, 1.5 mg) in acetonitrile (50 μL) was treated with triethylamine trihydrofluoride (50 μL) and one equivalent of methanolic HCl in a polyethylene vial. The reaction was stirred at room temperature overnight, then partitioned between EtOAc and 5% $NaHCO_3$. The organic layer was dried and evaporated to give **14**; ^1H NMR ($CDCl_3$, TMS) δ 8.17 (d, 2H); 7.61 (m, 1H); 7.49 (m, 2H); 5.86 (d, 1H, J = 5.1 Hz); 5.66 (d, 1H, J = 8.3 Hz); 5.15 (m, 1H); 4.51 (d, 1H, J = 8.5 Hz); 4.50 (m, 1H); 4.34 (d, 1H, J = 8.2 Hz); 4.30 (d, 1H, J = 8.2 Hz); 4.04 (m, 1H); 2.80 (d, 1H, J = 5.3 Hz); 2.55 (m, 1H); 2.53 (d, 1H, J = 16.3 Hz); 2.39 (m, 1H); 2.30 (bs, 1H); 2.25 (s, 3H); 2.13 (s+m, 4H); 1.86 (s+m, 2H); 1.69 (s, 3H); 1.19 (s, 3H); 1.09 (s, 3H); 1.04 (d, 3H, J = 7.1 Hz).

(12*R*)-10-Deacetyl-11,12-dihydrobaccatin III (15). A solution of (12*R*)-11,12-dihydrobaccatin III (1 mg) in 95% ethanol (80 μL) was treated with hydrazine hydrate (8μL). The reaction was stirred at RT six hours. The reaction was partitioned between EtOAc and 5% $NaHSO_4$, and the organic layer was dried and evaporated, giving **15**; ^1H NMR ($CDCl_3$, TMS) δ 8.09 (d, 2H); 7.54 (m, 1H); 7.41 (m, 2H); 5.57 (d, 1H, J = 8.3 Hz); 5.05 (m, 1H); 5.04 (d, 1H); 4.33 (d, 1H, J = 8.5 Hz); 4.26 (d, 1H, J =

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8.2 Hz); 4.21 (d, 1H, J = 8.2 Hz); 4.06 (m, 1H); 3.98 (m, 1H); 2.53 (m, 1H,); 2.42 (d, 1H, J = 16.1 Hz); 2.28 (m, 1H; 2.18 (s, 3H); 1.83 (m, 1H); 1.78 (m, 2H); 1.66 (s, 3H); 1.17 (d, 3H); 1.07 (s, 3H); 0.96 (s, 3H).

(12*R*)-7-O-Triethylsilyl-11,12-dihydrobaccatin III-13-(4S,5R)-N-(benzoyl)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidinecarboxylic Acid Ester. A suspension of (4S,5R)-N-(benzoyl)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidinecarboxylic acid potassium salt (91 mg of 75% salt, 1.5 mM) in EtOAc was washed with 5% aqueous $NaHSO_4$. The aqueous layer was re-extracted and the combined EtOAc solutions were dried over anhydrous Na_2SO_4 and evaporated to give the free acid as a thick oil. It was used immediately in the coupling reaction. (12*R*)-7-O-Triethylsilyl-11,12-dihydrobaccatin III (**13**, 70 mg, 0.10 mM) was treated with a solution of (4S,5R)-N-(benzoyl)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidinecarboxylic acid (0.15 mM) in CH_2Cl_2 (0.75 mL) and toluene (1.65 mL). Solid 4-dimethylaminopyridine (6.3 mg) and 1,3-dicyclohexylcarbodiimide (36.2 mg, 0.18 mM) were added and the reaction was put under an inert atmosphere. It was then heated to 75°C for 90 minutes. The reaction was cooled and filtered onto a column of silica gel 60 (10 g, 230-400 mesh) and eluted with (30-70) EtOAc-hexane and (30-70) EtOAc-toluene. Fractions of 4 mL were collected. The desired product as a mixture of diastereomers (26 mg) was found in fractions 33-41. It was further purified by column chromatography in acetone-hexane which gave pure product (0.021 g, 18%); ^{1}H NMR ($CDCl_3$, TMS) δ 8.05 (d, 2H); 7.20-7.65 (m, 14H); 6.67 (bs, 1H); 6.56 (d, 1H, J = 6.2 Hz); 6.35 (m, 2H); 5.69 (d, 1H, J = 8.0 Hz); 5.35 (bs, 1H); 4.88 (dd, 1H); 4.56 (m, 1H); 4.27 (m, 2H); 3.78 (s, 3H); 3.59 (m, 4H); 2.65 (m, 1H); 2.47 (d, 1H); 2.30 (m, 1H); 2.17 (m, 1H); 1.98 (s+m, 8H); 1.84 (s, 1H); 1.78 (m, 1H); 1.66 (s, 3H); 1.18 (s, 3H); 1.13 (s, 3H); 1.05 (d, 3H), 0.81 (m, 9H); 0.40 (m,

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6H); ^{13}C NMR ($CDCl_3$, TMS) δ 208.1, 170.4, 169.5, 167.8, 167.3, 161.2, 158.8, 136.6, 133.6, 129.9, 129.6, 129.2, 128.5, 128.3, 127.8, 127.6, 126.9, 117.9, 103.8, 98.3, 87.1, 83.0, 80.8, 78.0, 8.2, 75.0, 72.6, 70.6, 70.2, 58.0, 55.2, 55.0, 53.5, 41.4, 40.4, 36.3, 35.8, 33.6, 32.7, 24.9, 21.5, 21.0, 15.4, 14.7, 9.3, 6.8, 5.9; mass spectrum (FAB) [m+H]+ ion observed at m/z 1118, other ions at m/z 980, 434, 388, 165, 105.

Reaction of 7-O-Triethylsilyl-11,12-dihydrobaccatin III-13-(4S,5R)-N-(benzoyl)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidinecarboxylic Acid Ester with HCl/Methanol. Formation of 17. A solution of HCl in MeOH was prepared by adding acetyl chloride (35μL, 0.49 mM) to MeOH (10 mL) and allowing the solution to stand for 1.5 h. The product of the preceding reaction (20 mg, 0.018 mM) was treated with the HCl/MeOH for 14 minutes. The reaction was diluted with EtOAc and washed with 5% aqueous $NaHCO_3$. The EtOAc solution was dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified by column chromatography on silica gel 60 (3 g, 230-400 mesh) eluting with (20-80) acetone-hexane. Fractions of 1-2 mL were collected. The product (**17**) as a mixture of two diastereomers was isolated in fractions 11-17; ^1H NMR ($CDCl_3$, TMS) δ 7.77 (m, 2H); 7.22-7.61 (m, 14H); 6.30 (d, 1H, J = 5.6 Hz); 5.82 (dd, 1H); 5.30 (m, 1H); 5.24 (d, 1H); 4.88 (d, 1H, J = 8.7 Hz); 4.75 (dd, 1H); 4.66 (m, 2H); 4.51 (d, 1H, J = 7.6 Hz); 4.30 (d, 1H, J = 7.0 Hz); 3.29 (d, 1H, J = 7.5 Hz); 3.03 (s, 3H); 2.62 (m, 1H); 2.47 (m, 1H); 2.02 (s, 3H); 1.93 (m, 4H); 1.76 (s, 3H); 1.74 (s, 3H); 1.20 (s, 3H); 1.11 (s, 3H); 0.96 (m, 9H); 0.54 (m, 9H).

11,12-Dihydrotaxol (16). The product from the preceding reaction (**17**, 7 mg, 0.007 mM) was treated with (5:1) HOAc-H_2O and heated under an inert atmosphere to 50°C for 23 h. The reaction solution was concentrated by freeze-drying. The crude product was chromatographed on silica gel 60 (1 g, 230-400 mesh) eluting with (20-80) to (40-

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60) acetone-hexane. Fractions of 0.5-1 mL were collected. Fractions 19-22 contained product still having a 7-O-TES group. The desired product **16** (0.0037 g, 62%) was found in fractions 28-31; ^{1}H NMR ($CDCl_3$, TMS) δ 8.05 (d, 2H, J = 7.2 Hz); 7.78 (d, 2H, J = 7.0 Hz); 7.27-7.65 (m, 14H); 5.95 (dd, 1H); 5.89 (d, 1H); 5.72 (d, 1H); 5.60 (m, 1H); 5.10 (dd, 1H); 4.85 (dd, 1H); 4.48 (m, 1H); 4.30 (m, 3H); 3.49 (d, 1H); 2.79 (d, 1H); 2.60 (m, 1H); 2.48 (m, 1H); 2.38 (d, 1H); 2.24 (s, 3H); 2.17 (m, 1H); 1.99 (m, 2H); 1.85 (s, 3H); 1.74 (s, 3H); 1.25 (d, 1H); 1.13 (s, 3H); 1.08 (s, 3H); 0.50 (d, 3H); mass spectrum (FAB) 856.3572, $C_{47}H_{53}NO_{14}$ + H_1 requires 856.3544, other ions at m/z 796, 286, 122, 105.

(12*R*)-7-O-Triethylsilyl-11,12-dihydrobaccatin III-13-(4S,5R)-N-(BOC)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidinecarboxylic acid ester. A suspension of (4S,5R)-N-(BOC)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidine carboxylic acid potassium salt (154 mg of 78% pure potassium salt, 0.26 mM) in EtOAc was washed with 5% aqueous $NaHSO_4$. The EtOAc layer was dried over Na_2SO_4 and evaporated. The residue was combined with DMAP and added to (12*R*)-7-O-triethylsilyl-11,12-dihydro-baccatin III (**13**). The reaction was treated with DCC (60 mg, 0.29 mM) and stirred at RT overnight. The reaction was filtered onto a column of silica gel (10 g, 230-400 mesh) and eluted with (30-70) EtOAc-toluene. Fractions of 3 mL were collected. Starting material (45 mg, 67%) was recovered in fractions 12-17. Desired product diastereomers (0.047 g, 40%), not completely pure, were found in fractions 8-11; ^{1}H NMR ($CDCl_3$, TMS) δ 8.03 and 7.94 (2d, 2H); 7.59-7.00 (m, 11H); 6.4 (m, 4H); 6.16 (m, 1H); 5.62 (d, 1H); 5.44 (b, 1H); 4.85 (d+m, 2H); 4.61 (m, 2H); 4.39 (d, 1H); 4.21 (d, 1H); 3.84 (s's+m, 8H); 3.49 (m, 1H); 2.45 (d+m, 2H); 2.1-1.7 (m, 7H); 1.5-0.8 (m, 32H); 0.50 (m, 6H).

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(12*R*)-13-(N-*t*-Butoxycarbonyl-β-phenylisoserinyl)-11,12-dihydrobaccatin III (18). A solution of (12*R*)-7-O-triethylsilyl-11,12-dihydrobaccatin III-13-(4S,5R)-N-(BOC)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidinecarboxylic acid ester (46 mg, 0.04 mM) in 3 mL of (80-20) acetic acid-water was stirred at room temperature for 3 days. The reaction was partitioned between EtOAc and 5% aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4 and evaporated. Since deprotection was not yet complete, the residue was treated with 0.2 N HCl in methanol (2 mL) for 35 min. Water (0.13 mL) was added and the reaction was stirred 25 min longer. The reaction was worked up as above. The crude product was purified by column chromatography on silica gel 60 (5 g, 230-400 mesh) in acetone-toluene mixtures. Fractions of 2 mL were collected. The desired product (**18**, 6 mg, 17%) was found in fractions 15-21; ^1H NMR ($CDCl_3$, TMS) δ 8.07 (d, 2H); 7.62 (m, 1H); 7.50-7.30 (m, 7H); 6.02 (d, 1H); 5.75 (d, 1H, J = 8.3 Hz); 5.61 (m, 2H); 5.36 (m, 1H); 5.08 (d, 1H J = 8.4 Hz); 4.66 (m, 1H); 4.48 (m, 1H); 4.32 (AB, 2H); 4.05 (m, 1H); 3.51 (d, 1H, J = 8.3 Hz); 2.88 (m, 1H); 2.59 (m, 2H); 2.39 (d, 1H, J = 17.5 Hz); 2.22 (2s+m, 8H); 1.93 (m, 1H); 1.86 (s, 1H); 1.76 (s, 3H); 1.39 (s, 9H); 1.20 (s, 3H); 1.13 (s, 3H); 0.85 (d, 3H); mass spectrum (FAB) 852.3813, $C_{45}H_{57}N_1O_{15} + H_1$ requires 852.3806.

7-O-Triethylsilyl-11,12-dihydro-12-hydroxy-baccatin III-13-(4S,5R)-N-(BOC)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidinecarboxylic acid ester. A suspension of (4S,5R)-N-(BOC)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-oxazolidine-carboxylic acid potassium salt (61.4 mg of 74% pure potassium salt, 0.097 mM) in EtOAc was washed with 5% aqueous $NaHSO_4$. The aqueous layer was re-extracted twice, and the combined EtOAc solutions were dried over anhydrous Na_2SO_4 and evaporated to give the free acid (**9**) as a thick oil. It was used immediately in the

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coupling reaction. Alcohol **8** (32 mg, 0.045 mM) was treated with a solution of **9** (0.097 mM) in CH_2Cl_2 (0.3 mL) and toluene (0.7 mL). Solid 4-dimethylaminopyridine (4.3 mg) and 1,3-dicyclohexylcarbodiimide (23 mg, 0.11 mM) were added and the reaction stirred at room temperature for 3 h. The reaction was diluted with EtOAc and washed with dilute aqueous $NaHSO_4$, water, and brine. The EtOAc solution was dried over anhydrous Na_2SO_4 and evaporated. The crude product (106 mg) was dissolved in (30-70) acetone-hexane, filtered onto a column of silica gel 60 (6 g, 230-400 mesh), and eluted with (30-70) acetone-hexane. Fractions of 2 mL were collected. The desired product as a mixture of diastereomers (0.0454 g, 89%) was found in fractions 16-24. ^1H NMR ($CDCl_3$, TMS) δ 8.08 (m, 2H); 7.1-7.7 (m, 13H); 6.7 (b, 1H); 6.5 (m, 2H); 5.7 (m, 1H); 5.3 (m, 1H); 4.9 (m, 1H); 4.7 (m, 1H); 4.4 (m, 2H); 3.8 (m, 7H); 3.5 (m, 1H); 2.5 (m, 1H); 2.1 (m, 4H); 1.6-2.1 (m, 8H); 1.1-1.5 (s's, 6H); 1.05 (s's, 9H); 0.93 (m, 12H); 0.52 (m, 6H); mass spectrum (FAB) [m+H] ion observed at m/z 1130, other ions at m/z 1030, 1012, 970, 330, 284, 105.

13-(N-t-butoxycarbonyl-β-phenylisoserinyl)-11,12-dihydro-12-(S)-hydroxybaccatin III (19). The product from the preceding experiment (40 mg, 0.035 mM) was treated with (4:1) HOAc-H_2O (3 mL) and stirred at room temperature for 8 days. The reaction was diluted with EtOAc and washed with 5% aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 and evaporated. The crude product was chromatographed on silica gel 60 (10 g, 230-400 mesh) eluting with (20-80) to (50-50) EtOAc-hexane followed by (40-60) acetone-hexane. Fractions of 5 mL were collected. The desired product, still not completely pure, was obtained from fractions 74-83 (14.4 mg). This material was rechromatographed on silica gel (3 g) in (40-60) acetone-hexane. Fractions of 0.5-1 mL were collected. The product (0.011 g, 36%) was isolated

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in fractions 23-29; ^{1}H NMR ($CDCl_3$, TMS) δ 8.14 (d, 2H, J = 7.1 Hz); 7.60 (m, 1H); 7.50 (m, 2H); 7.35 (m, 5H); 5.77 (d, 1H, J = 7.4 Hz); 5.55 (m, 1H); 5.35 (m, 1H); 5.25 (m, 1H); 5.01 (m, 1H); 4.59 (bs, 1H); 4.49 (m, 1H); 4.44 (d, 1H, J = 8.8 Hz); 4.36 (d, 1H, J = 8.5 Hz); 3.67 (bs, 1H); 3.46 (d, 1H); 3.31 (bs, 1H); 2.76 (d, 1H, J = 5.1 Hz); 2.61 (d, 1H, J = 5.7 Hz); 2.55 (m, 1H); 2.43 (s, 3H); 2.17 (s, 3H); 2.01 (m, 3H); 1.89 (s, 1H); 1.67 (s, 3H); 1.43 (s, 3H); 1.23 (s, 9H); 1.17 (s, 3H); 1.08 (s, 3H); ^{13}C NMR ($CDCl_3$, TMS) δ 207.2, 174.8, 172.1, 171.1, 166.8, 155.2, 138.4, 133.7, 130.2, 129.1, 128.9, 128.8, 128.2, 126.6, 84.2, 81.7, 81.4, 80.4, 78.3, 77.3, 76.6, 74.5, 74.0, 68.9, 61.4, 58.2, 56.3, 41.2, 40.2, 34.8, 34.4, 33.2, 28.1, 27.4, 22.3, 22.0, 21.2, 11.0; mass spectrum (FAB) 868.3763, $C_{45}H_{57}NO_{16} + H_1$ requires 868.3755, other ions at m/z 768, 708, 587, 405, 105.

Additional References

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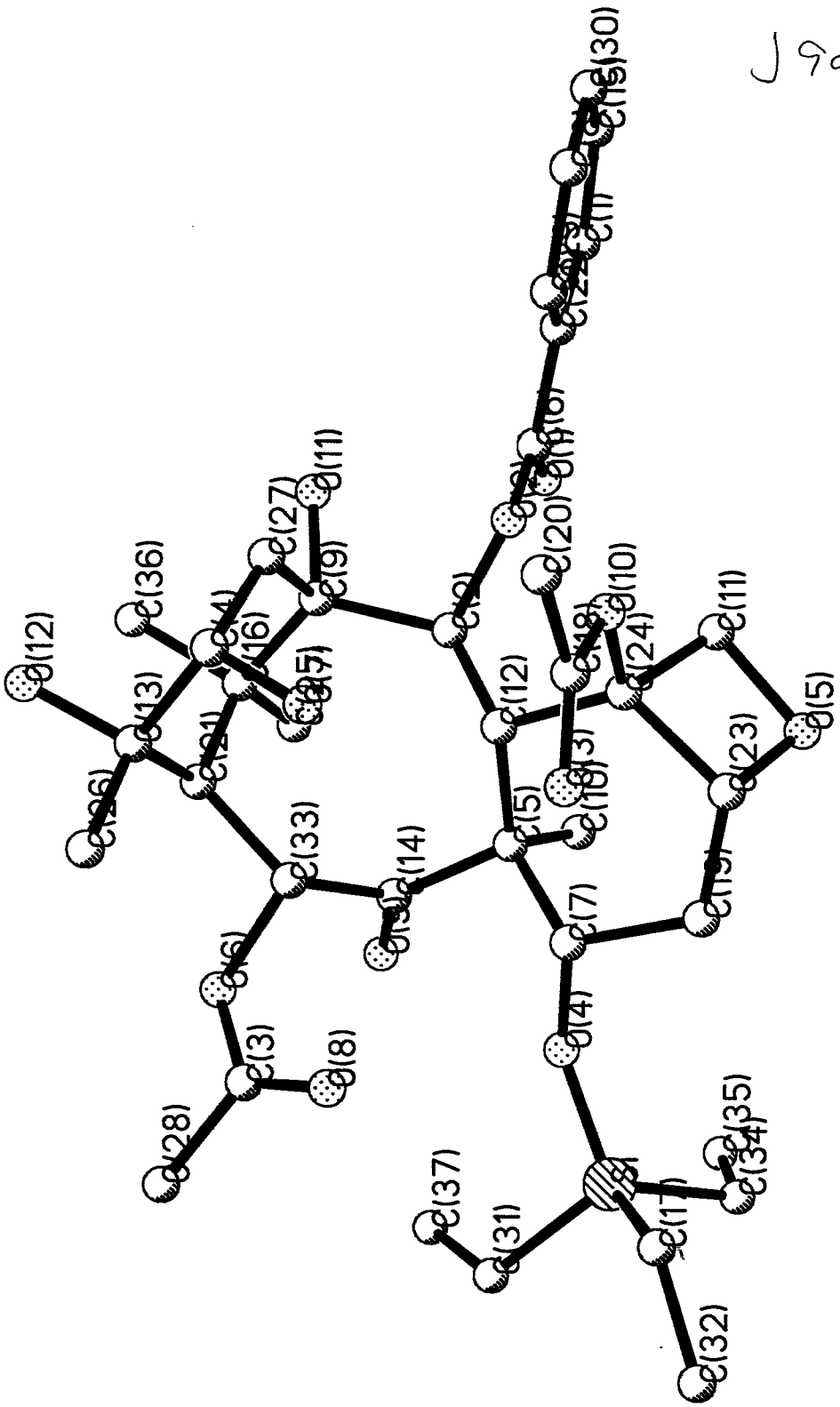

ORTEP drawing of the structure of compound 8.

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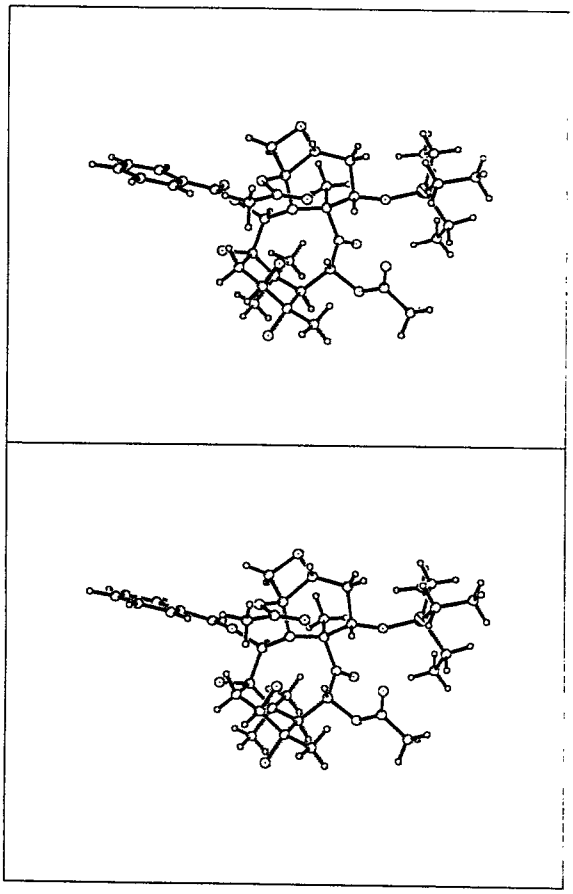

Stereoscopic representation of the structure of compound 8.

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Table 1. Fractional coordinates (x10⁴) and Beq(Å²)
Estimated standard deviations are in parentheses.
Beq = 4/3($a^2B_{11}+b^2B_{22}+c^2B_{33}+abcos\gamma B_{12}+accos\beta B_{13}+bccos\alpha B_{23}$)

	x	y	z	B
SI	9349(5)	3068(2)	9083(1)	2.46(8)
O(1)	16140(11)	3986(5)	7139(3)	2.14(17)
O(2)	13925(10)	4732(5)	7163(2)	1.98(17)
O(3)	8852(11)	4974(5)	7578(3)	2.32(18)
O(4)	10587(12)	3497(5)	8760(3)	3.02(20)
O(5)	10978(12)	2785(5)	7357(3)	2.84(19)
O(6)	12142(11)	5719(5)	9040(3)	2.26(18)
O(7)	10949(11)	6345(5)	7760(3)	2.17(17)
O(8)	9511(13)	5384(6)	8956(3)	3.79(23)
O(9)	13457(11)	4290(5)	8921(3)	2.53(18)
O(10)	10809(11)	4651(5)	7128(3)	2.14(17)
O(11)	16039(11)	5674(5)	7455(2)	2.14(17)
O(12)	14041(11)	7517(5)	8284(3)	2.48(18)
C(1)	16526(18)	4414(8)	6254(4)	3.0(3)
C(2)	13948(16)	4777(7)	7639(4)	1.57(22)
C(3)	10646(20)	5647(9)	9169(4)	3.3(3)
C(4)	12423(17)	6757(7)	7803(4)	1.95(24)
C(5)	12347(17)	4058(8)	8222(4)	2.11(25)
C(6)	15243(16)	4430(8)	6964(4)	2.09(26)
C(7)	10573(18)	3851(8)	8334(4)	2.51(28)
C(8)	14188(22)	5375(10)	5907(5)	4.4(3)
C(9)	14627(16)	5651(7)	7727(4)	1.76(24)
C(10)	13300(17)	3288(8)	8211(4)	2.59(29)
C(11)	12211(17)	3356(8)	7199(4)	2.54(28)
C(12)	12332(16)	4558(7)	7788(4)	1.91(24)
C(13)	12887(17)	6874(8)	8272(4)	2.53(28)
C(14)	12891(17)	4567(8)	8601(4)	2.65(29)
C(15)	16714(19)	4647(9)	5851(5)	3.5(3)
C(16)	15109(16)	5806(8)	8181(4)	2.09(26)
C(17)	7220(19)	3292(9)	8965(5)	3.4(3)
C(18)	9515(17)	5091(8)	7253(4)	2.35(26)
C(19)	9764(17)	3255(8)	8021(4)	2.72(29)
C(20)	9127(18)	5701(8)	6924(4)	2.68(27)
C(21)	13784(17)	6109(7)	8455(4)	2.07(25)
C(22)	15199(16)	4668(8)	6511(4)	2.16(26)
C(23)	10095(17)	3422(8)	7567(4)	2.55(28)
C(24)	11446(16)	4057(7)	7446(4)	2.20(26)
C(25)	15960(18)	5056(8)	8378(4)	2.50(27)
C(26)	11480(18)	7199(8)	8532(4)	2.86(29)
C(27)	13686(16)	6354(7)	7540(4)	1.89(24)
C(28)	10414(20)	5950(9)	9604(5)	3.6(3)
C(29)	14055(19)	5154(9)	6333(4)	3.2(3)
C(30)	15580(22)	5123(10)	5681(5)	4.2(3)
C(31)	9764(20)	3464(10)	9620(5)	3.9(3)
C(32)	6060(24)	2944(11)	9278(6)	5.7(4)
C(33)	12452(18)	5494(8)	8587(4)	2.57(28)
C(34)	9660(19)	1918(9)	9074(5)	3.4(3)
C(35)	11175(23)	1632(11)	9129(6)	5.9(4)

C(36)	16446(17)	6464(8)	8185(4)	2.27(26)
C(37)	11564(22)	3488(11)	9758(5)	5.0(4)
(W1)	8456(9)	4854(4)	4689(2)	0.70(13)
(W2)	10883(13)	4702(6)	5319(3)	2.84(20)
(T1)	6945(20)	2298(10)	4149(5)	2.7(3)
(T2)	9887(28)	2525(12)	4525(5)	3.3(3)
(T3)	10265(26)	4978(13)	4773(6)	7.0(5)
(T4)	10822(18)	4288(8)	5245(4)	2.33(27)
(T5)	10894(29)	2417(12)	4574(6)	5.6(4)
(T6)	8874(27)	1970(13)	4169(7)	7.5(5)
(T7)	7589(39)	2599(17)	4388(9)	10.2(7)
(T9)	9130(34)	2749(15)	4535(7)	6.8(6)
(T10)	6749(22)	2026(11)	4015(5)	3.6(4)

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Table 2. Bond lengths(Å) and angles(°)

A. Bond lengths(Å)

SI O(4)	1.629(10)	C(8) C(30)	1.446(25)
SI C(17)	1.892(17)	C(9) C(16)	1.512(17)
SI C(31)	1.849(16)	C(9) C(27)	1.530(18)
SI C(34)	1.915(15)	C(11) C(24)	1.540(18)
O(1) C(6)	1.194(16)	C(12) C(24)	1.556(18)
O(2) C(2)	1.502(14)	C(13) C(21)	1.585(19)
O(2) C(6)	1.380(16)	C(13) C(26)	1.550(20)
O(3) C(18)	1.187(16)	C(14) C(33)	1.574(19)
O(4) C(7)	1.467(16)	C(15) C(30)	1.358(23)
O(5) C(11)	1.497(17)	C(16) C(21)	1.508(19)
O(5) C(23)	1.454(17)	C(16) C(25)	1.563(19)
O(6) C(3)	1.346(19)	C(16) C(36)	1.574(19)
O(6) C(33)	1.499(16)	C(17) C(32)	1.512(24)
O(7) C(4)	1.437(16)	C(18) C(20)	1.482(18)
O(8) C(3)	1.257(19)	C(19) C(23)	1.484(19)
O(9) C(14)	1.207(16)	C(21) C(33)	1.580(19)
O(10) C(18)	1.380(17)	C(22) C(29)	1.383(20)
O(10) C(24)	1.502(15)	C(23) C(24)	1.604(19)
O(11) C(9)	1.479(15)	C(31) C(37)	1.598(25)
O(12) C(13)	1.448(17)	C(34) C(35)	1.388(25)
C(1) C(15)	1.337(20)	(W1) (T3)	1.581(23)
C(1) C(22)	1.454(20)	(W2) (T4)	0.724(17)
C(2) C(9)	1.577(17)	(T1) (T6)	1.735(29)
C(2) C(12)	1.502(19)	(T1) (T7)	1.056(34)
C(3) C(28)	1.473(20)	(T1) (T10)	0.637(24)
C(4) C(13)	1.544(18)	(T2) (T5)	0.891(34)
C(4) C(27)	1.515(18)	(T2) (T6)	1.686(30)
C(5) C(7)	1.593(21)	(T2) (T9)	0.745(36)
C(5) C(10)	1.509(19)	(T5) (T9)	1.607(37)
C(5) C(12)	1.595(17)	(T6) (T7)	1.659(38)
C(5) C(14)	1.534(19)	(T6) (T9)	1.739(32)
C(6) C(22)	1.483(17)	(T7) (T9)	1.417(43)
C(7) C(19)	1.554(19)	(T7) (T10)	1.669(35)
C(8) C(29)	1.396(21)		

B. Bond angles(°)

O(4) SI C(17)	114.6(6)	C(21) C(16) C(25)	112.5(10)
O(4) SI C(31)	107.1(6)	C(21) C(16) C(36)	108.2(10)
O(4) SI C(34)	109.3(6)	C(25) C(16) C(36)	101.8(11)
C(17) SI C(31)	107.1(7)	SI C(17) C(32)	115.3(11)
C(17) SI C(34)	108.9(7)	O(3) C(18) O(10)	122.9(12)
C(31) SI C(34)	109.7(7)	O(3) C(18) C(20)	127.5(13)
C(2) O(2) C(6)	117.5(9)	O(10) C(18) C(20)	109.6(11)
SI O(4) C(7)	137.7(9)	C(7) C(19) C(23)	114.1(11)
C(11) O(5) C(23)	93.5(9)	C(13) C(21) C(16)	114.7(10)
C(3) O(6) C(33)	115.7(10)	C(13) C(21) C(33)	105.0(11)

Table 3. Close intermolecular contacts between non-hydrogen atoms. Symmetry operations listed were performed on the first atom. Distances are in Å.

O(1).....O(3)	x-1, y, z	3.152(12)
O(1).....C(18)	x-1, y, z	3.429(17)
O(9).....C(32)	x-1, y, z	3.337(21)
O(11)....O(3)	x-1, y, z	2.693(13)
O(11)....C(18)	x-1, y, z	3.184(17)
O(11)....C(20)	x-1, y, z	3.124(17)
O(8).....(W1)	11/2-x, 1-y, z-1/2	3.452(13)
C(26)....(T10)	11/2-x, 1-y, z-1/2	3.398(23)
O(6).....(T3)	21/2-x, 1-y, z-1/2	3.400(23)
O(9).....(T3)	21/2-x, 1-y, z-1/2	3.141(22)
O(12)....(T6)	21/2-x, 1-y, z-1/2	3.417(23)
O(7).....O(5)	2-x, y-1/2, 11/2-z	2.913(13)
C(4).....O(5)	2-x, y-1/2, 11/2-z	3.400(17)
O(12)....O(1)	3-x, y-1/2, 11/2-z	2.769(12)
O(12)....C(1)	3-x, y-1/2, 11/2-z	3.485(16)
O(12)....C(6)	3-x, y-1/2, 11/2-z	3.307(15)
C(1).....(T6)	x-1/2, 1/2-y, 1-z	3.482(27)
(T4).....(T1)	x-1/2, 1/2-y, 1-z	3.379(22)
(T4).....(T10)	x-1/2, 1/2-y, 1-z	3.281(22)

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C(18) O(10) C(24)	116.3(9)	C(16) C(21) C(33)	118.6(10)
C(15) C(1) C(22)	122.6(14)	C(1) C(22) C(6)	116.1(12)
O(2) C(2) C(9)	103.1(9)	C(1) C(22) C(29)	119.5(12)
O(2) C(2) C(12)	106.9(10)	C(6) C(22) C(29)	124.2(12)
C(9) C(2) C(12)	120.1(10)	O(5) C(23) C(19)	113.8(11)
O(6) C(3) O(8)	126.9(12)	O(5) C(23) C(24)	89.4(10)
O(6) C(3) C(28)	112.3(13)	C(19) C(23) C(24)	119.3(11)
O(8) C(3) C(28)	120.8(15)	O(10) C(24) C(11)	107.9(10)
O(7) C(4) C(13)	111.9(10)	O(10) C(24) C(12)	107.0(9)
O(7) C(4) C(27)	111.4(10)	O(10) C(24) C(23)	108.9(10)
C(13) C(4) C(27)	113.4(11)	C(11) C(24) C(12)	122.9(12)
C(7) C(5) C(10)	109.7(11)	C(11) C(24) C(23)	86.3(9)
C(7) C(5) C(12)	107.0(10)	C(12) C(24) C(23)	122.0(10)
C(7) C(5) C(14)	103.4(10)	C(4) C(27) C(9)	119.7(10)
C(10) C(5) C(12)	114.9(10)	C(8) C(29) C(22)	119.0(14)
C(10) C(5) C(14)	108.3(11)	C(8) C(30) C(15)	124.0(14)
C(12) C(5) C(14)	112.8(10)	SI C(31) C(37)	116.3(11)
O(1) C(6) O(2)	122.3(11)	O(6) C(33) C(14)	104.9(10)
O(1) C(6) C(22)	128.5(12)	O(6) C(33) C(21)	102.7(10)
O(2) C(6) C(22)	108.8(11)	C(14) C(33) C(21)	117.4(12)
O(4) C(7) C(5)	106.3(11)	SI C(34) C(35)	117.6(12)
O(4) C(7) C(19)	109.5(10)	(T6) (T1) (T7)	68.0(21)
C(5) C(7) C(19)	114.7(11)	(T6) (T1) (T10)	93.1(25)
C(29) C(8) C(30)	117.7(15)	(T7) (T1) (T10)	159.7(34)
O(11) C(9) C(2)	102.8(9)	(T5) (T2) (T6)	120.0(22)
O(11) C(9) C(16)	108.8(10)	(T5) (T2) (T9)	158.2(35)
O(11) C(9) C(27)	100.7(9)	(T6) (T2) (T9)	81.5(26)
C(2) C(9) C(16)	115.0(10)	(T2) (T5) (T9)	9.9(16)
C(2) C(9) C(27)	115.5(10)	(T1) (T6) (T2)	110.1(15)
C(16) C(9) C(27)	112.3(10)	(T1) (T6) (T7)	36.2(13)
O(5) C(11) C(24)	90.4(10)	(T1) (T6) (T9)	85.1(15)
C(2) C(12) C(5)	112.7(11)	(T2) (T6) (T7)	74.0(16)
C(2) C(12) C(24)	110.9(10)	(T2) (T6) (T9)	25.1(12)
C(5) C(12) C(24)	108.8(10)	(T7) (T6) (T9)	49.2(16)
O(12) C(13) C(4)	106.8(10)	(T1) (T7) (T6)	75.8(21)
O(12) C(13) C(21)	104.2(11)	(T1) (T7) (T9)	143.1(31)
O(12) C(13) C(26)	105.2(10)	(T1) (T7) (T10)	7.6(13)
C(4) C(13) C(21)	111.9(10)	(T6) (T7) (T9)	68.3(19)
C(4) C(13) C(26)	110.5(11)	(T6) (T7) (T10)	68.8(15)
C(21) C(13) C(26)	117.3(11)	(T9) (T7) (T10)	136.8(24)
O(9) C(14) C(5)	124.4(12)	(T2) (T9) (T5)	11.9(20)
O(9) C(14) C(33)	119.1(12)	(T2) (T9) (T6)	73.5(24)
C(5) C(14) C(33)	115.9(11)	(T2) (T9) (T7)	134.8(33)
C(1) C(15) C(30)	117.1(15)	(T5) (T9) (T6)	85.2(16)
C(9) C(16) C(21)	113.3(11)	(T5) (T9) (T7)	146.7(22)
C(9) C(16) C(25)	111.6(10)	(T6) (T9) (T7)	62.4(17)
C(9) C(16) C(36)	108.8(10)	(T1) (T10) (T7)	12.7(21)